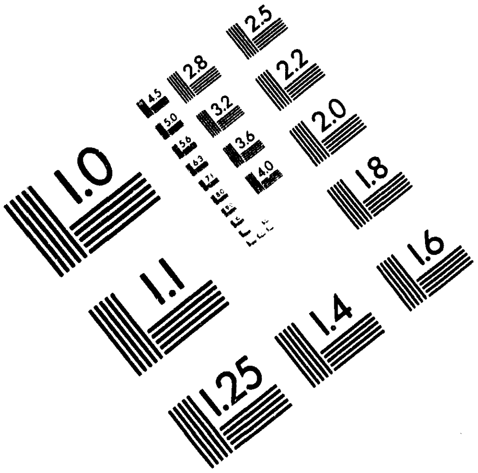

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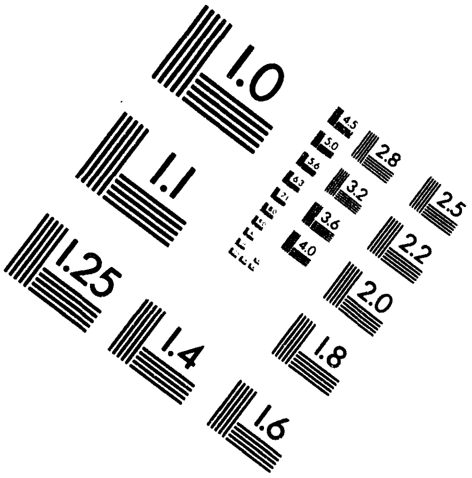

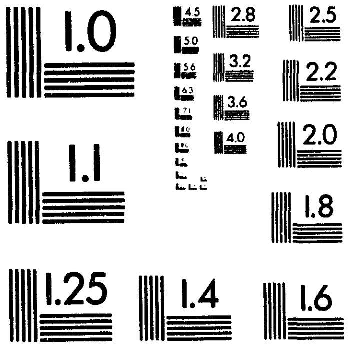

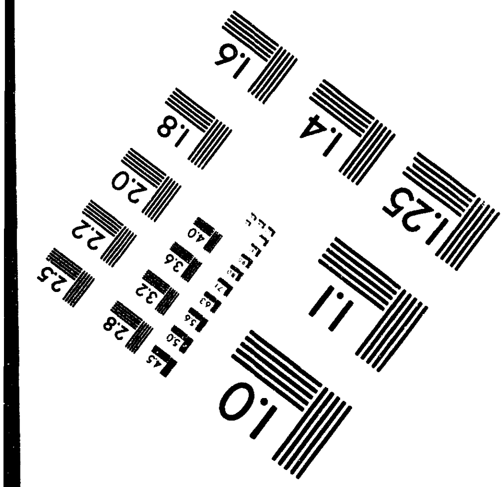

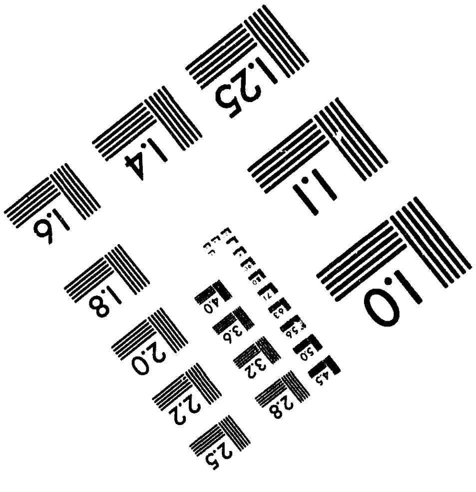

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QUARTERLY TECHNICAL PROGRESS REPORT

Title	Surfactant Loss Control in Chemical Flooding: Spectroscopic and Calorimetric Study of Adsorption and Precipitation on Reservoir Minerals
Contract no.	DE-AC22-92BC14884
University	Columbia University in the city of New York Box 20, Low Memorial Library New York, NY 10027.
Date of report	5/31/94
Contract date	9/30/92
Anticipated Completion Date	9/29/95
Government award	$ 602,232 ($ 195,019 for current year)
Program Manager	Prof. P. Somasundaran
Principal Investigator	Prof. P. Somasundaran
Contracting Officer's Representative	Dr. Jerry F. Casteel U.S. Department of Energy, Bartlesville Project Office, P.O. Box 1398, Bartlesville, OK 74005.
Reporting Period	1/1/94 to 3/31/94

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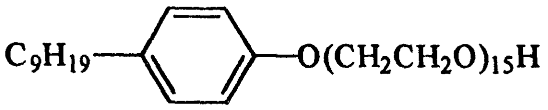
Summary of Technical Progress

Since surfactants are often present as mixtures, effort is being made to understand the synergetic and competitive forces involving determining adsorption of surfactants from their mixtures. Adsorption of tetradecyl trimethyl ammonium chloride (TTAC) and polyethoxylated nonyl phenol (NP-15) surfactant mixture at the alumina-water interface was studied during this reporting period. It was found that the nonionic surfactant NP-15 does not adsorb on alumina by itself, but was forced to adsorb by cationic TTAC. The adsorption density and the nature of adsorption isotherm of NP-15 were markedly dependent upon the quantity of TTAC present in the mixture and the procedure of surfactant addition. In the low concentration range the adsorption of both TTAC and NP-15 was enhanced by coadsorption, but in the high concentration range the adsorption of TTAC was depressed due to the competitive adsorption and steric hindrance.

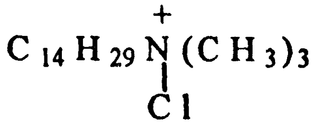
Electrokinetic behavior of alumina suspensions was also monitored along with the adsorption in order to delineate the role of electrostatic force in determining the mechanism of adsorption. Surface tension of surfactant mixtures before and after adsorption was measured to obtain information needed for developing mechanisms.

Adsorption of surfactant mixtures at alumina-water interface

In our previous reports the adsorption/desorption behavior of tetradecyl trimethyl ammonium chloride(TTAC) at the alumina-water interface has been reported. During this reporting we have initiated adsorption studies with surfactant mixtures. The generic structures of surfactant studied are shown in figure 1. The adsorption isotherm of TTAC on alumina at pH 10 and changes in zeta potential of alumina as a result of TTAC adsorption are shown in figure 2. It can be seen that TTAC adsorbs significantly at the alumina-water interface at pH 10. At this pH the alumina surface is negatively charged and electrostatic attraction with the cationic TTAC will be dominant. There is a sharp increase in the adsorption density around $5x10^{-4}$ kmol/m^3 which can attributed to formation of surfactant aggregates(hemimicelle) at the solid-liquid interface. Comparing zeta potential to the adsorption isotherm at the same residual concentrations, it can be seen that the charge of alumina is neutralized at a very low adsorption density. The maximum adsorption density of TTAC on alumina at pH 10 is about $2.5x10^{-6}$mol/m^2. This translates to roughly 66A^{o2}/molecule which is similar to the molecular area at air/solution interface(61A^{o2}) reported in literature[1]. This suggests that the adsorption layer at alumina is mainly monolayer. The settling rate of the alumina suspensions after TTAC adsorption at pH 10



a. Polyethoxylated nonyl phenol (NP-15)



$$C_{14}H_{29}\underset{\underset{Cl}{|}}{\overset{+}{N}}(CH_3)_3$$

b. Tetradecyl trimethyl ammonium chloride (TTAC)

Figure 1. Molecule structure of the surfactants studied

was measured and the results are shown in figure 3. In the absence of and at low surfactant adsorption, the alumina suspension in water is dispersed and the settling rate is low. Once the surfactant forms aggregates at the interface, the alumina surface becomes hydrophobic and the settling rate is markedly increased. With further increase in the TTAC adsorption, the settling rate decreases; this can be attributed to the increase the positive charge of alumina at higher surfactant

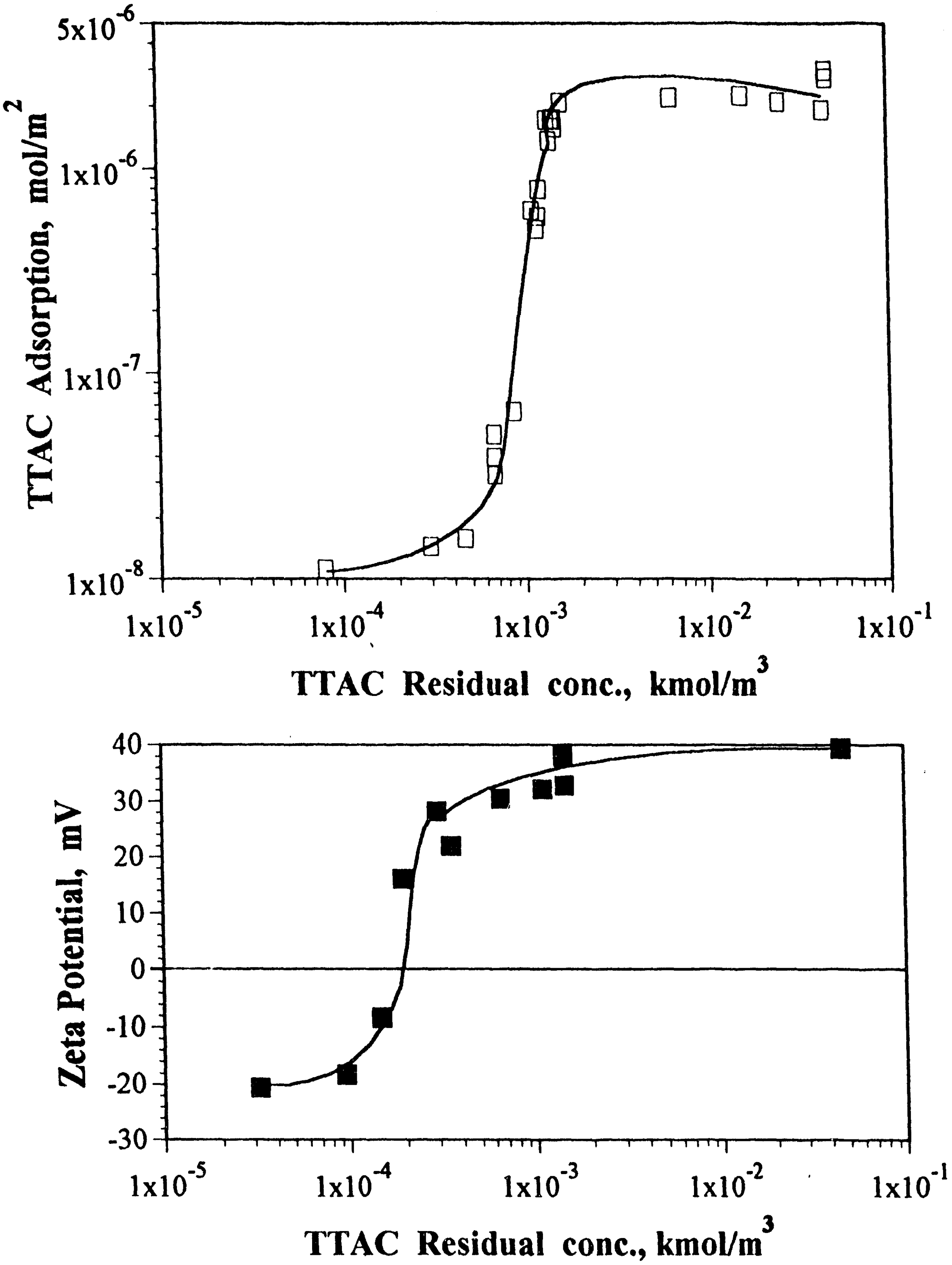


Figure 2. Adsorption of TTAC alone on alumina at pH=10 and zeta potential of alumina after adsorption

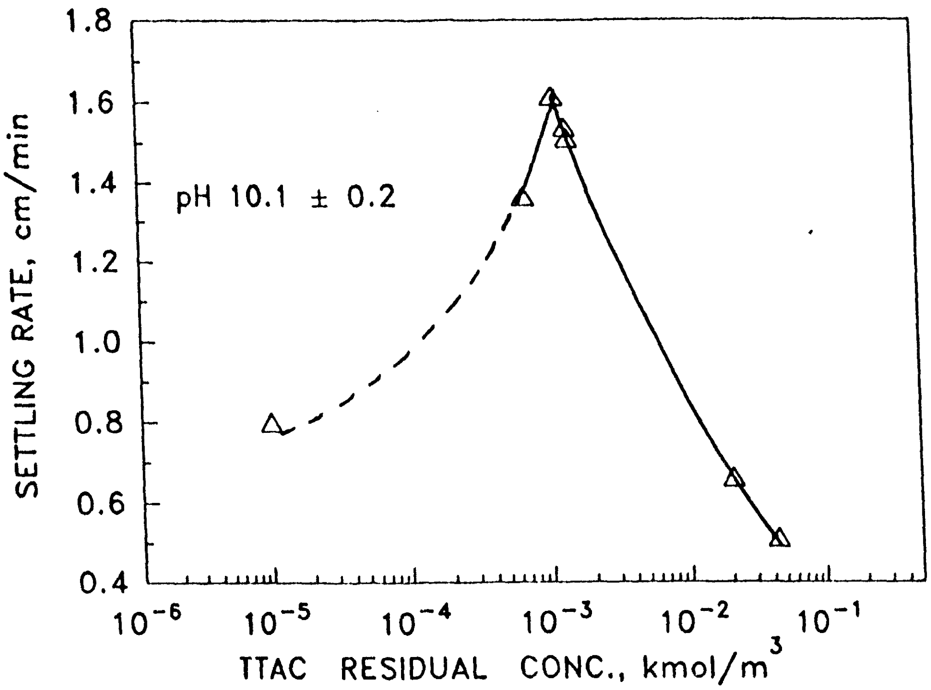


Figure 3 Settling rate of alumina suspension after TTAC adsorption at pH 10

concentration(zeta potential) causing repulsion between alumina particles. As a result of balance between hydrophobic attraction force and the electrical repulsion force, the settling rate reaches a maximum at a concentration of about 1×10^{-3}kmol/m^3. Above this concentration the settling rate decreases, making the electrostatic force dominant in this system at high concentration.

Figure 4 shows the adsorption isotherms of polyethoxylated nonyl phenol with 15 ethylene oxide groups (NP-15) on alumina in the presence of pre-adsorbed TTAC and when added together with TTAC. In all these experiments the initial concentration of TTAC was fixed, and the pH was maintained at 10. The experimental results showed that NP-15 does not adsorb on alumina by itself, even though at very high concentrations (around 1×10^{-2}kmol/m^3), there may have been some adsorption from solution, possibly due to surface precipitation in this concentration , this phenomenon merits further investigation.

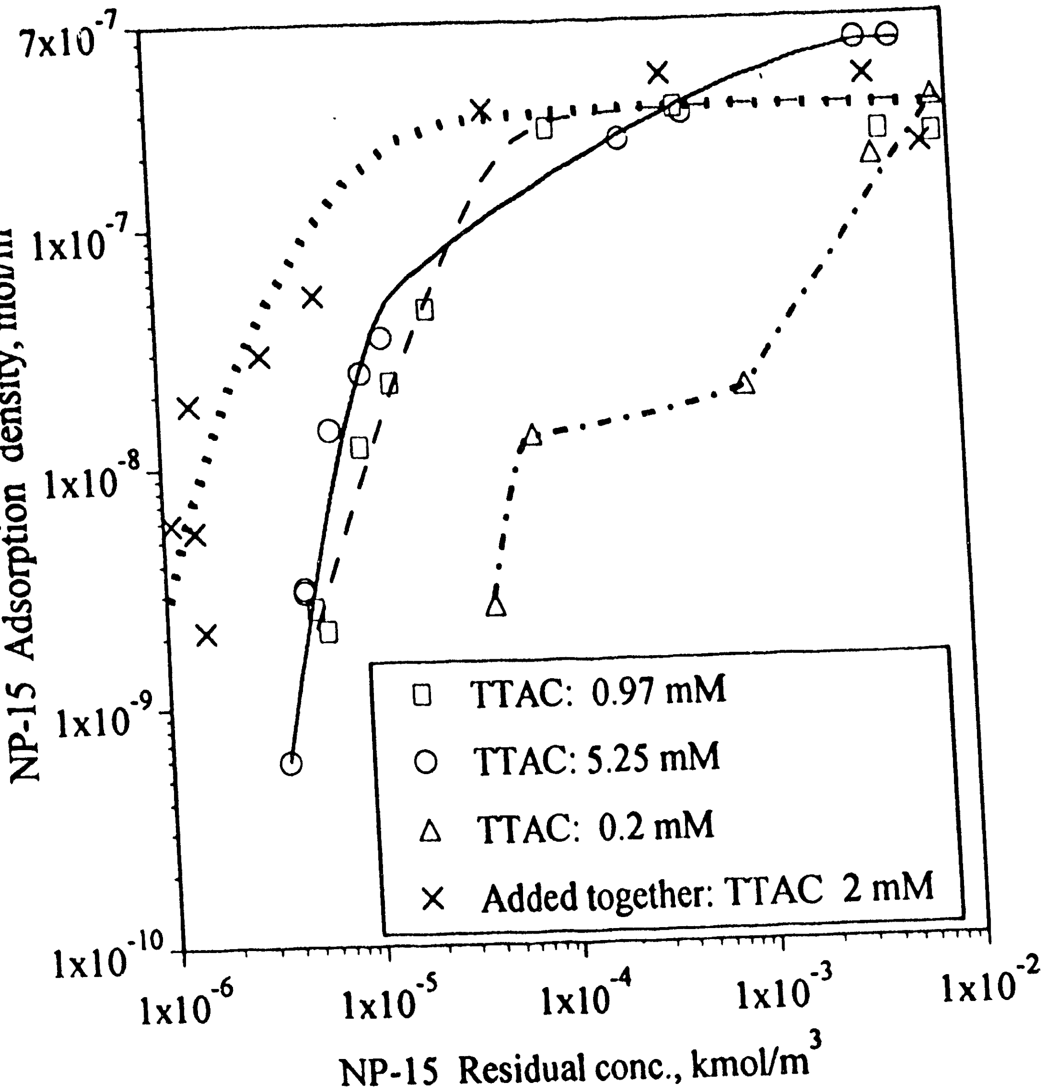


Figure 4. Adsorption isotherms of NP-15 on alumina with pre-adsorbed TTAC and/or with TTAC added together

It is interesting to note that tetradecyl trimethyl ammonium chloride does force the adsorption of NP-15 on alumina. Pre-adsorbed TTAC functions as anchors for the adsorption of NP-15. With an increase in TTAC initial concentration, the adsorption of NP-15 increased and the adsorption isotherms shifted to lower NP-15 concentrations. It is also observed that above a TTAC concentration at which it forms hemimicelle at the alumina-water interface there is no further effect on the adsorption of NP-15. It is interesting to note the implication that TTAC hemimicelles are impermeable by the NP-15 even though there is synergism between the two species. It will be important to test this and investigate the reasons for this behavior. Desorption and reorientation of surfactants adsorbed in the form of aggregates will depend to large extent on the activation barrier involved in dehemimicellisation. The results also show that the order of addition of the surfactants has a marked effect on the adsorption of NP-15. If NP-15 and TTAC were pre-mixed and added to the alumina suspension together, the adsorption density of NP-15 is higher, particularly in the low concentration range. This indicates that NP-15 adsorption from mixtures with TTAC is not completely reversible, but is controlled by the nature of molecule packed at the alumina-water interface. In other words, competition between TTAC and NP-15 for common adsorption sites and the resultant steric hindrance would affect the adsorption of NP-15, especially in the low concentration range. Particle wettability and dispersion can also expected to be affected by this markedly.

The adsorption isotherms of tetradecyl trimethyl ammonium chloride (TTAC) and polyethoxylated nonyl phenol (NP-15) on alumina from their 1:1 initial molar ratio mixture are given in Figures 5 and 6 respectively. The zeta potentials of alumina particles after surfactant mixture adsorption are also shown in figure 5.

Comparing the adsorption isotherms of TTAC and NP-15 in figure 5, it is seen that the adsorption of TTAC is higher at low concentrations. But the adsorption of NP-15 increase quickly with the increasing of the concentration , and soon reaches the same level as the adsorption of TTAC. At low concentration the TTAC molecules are attracted to the negatively charged surface but NP-15 is not. The adsorption of NP-15 is dependent on the pre-adsorbed or co-adsorbed TTAC acting as

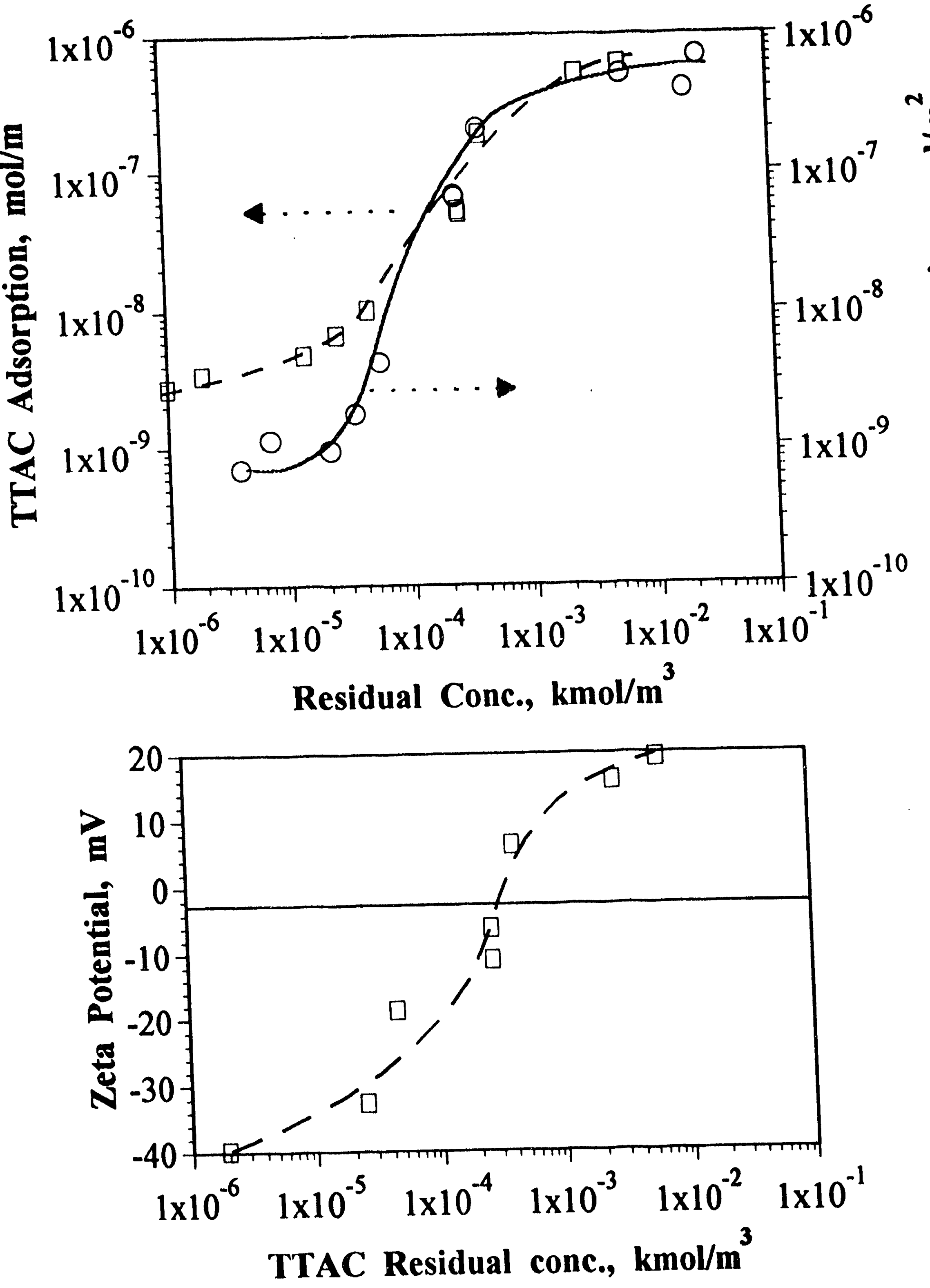


Figure 5. **Adsorption isotherms from 1:1 initial molar ratio mixture solution and the zeta potential of alumina after adsorption.**

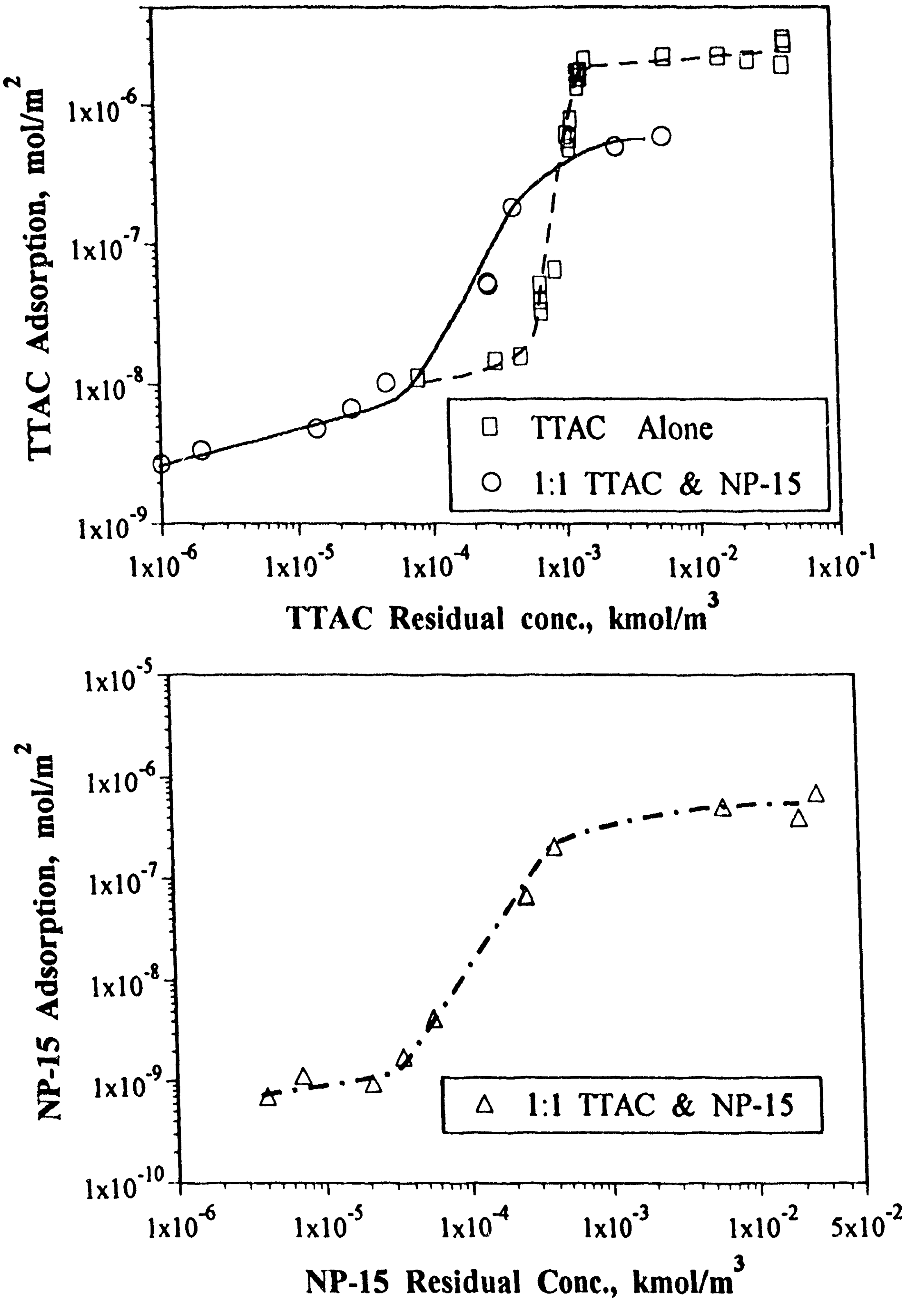


Figure 6. Adsorption of TTAC and NP-15 from 1:1 molar ratio mixture solution

anchors for the former by hydrophobic chain-chain interactions.

NP-15 is much larger and more hydrophobic than TTAC. The adsorption of NP-15 on the surface will provide steric hindrance to the packing of the molecules into aggregates. This can be seen from figure 6. The maximum adsorption density is apparently lower than the adsorption from TTAC alone. This may be explained by considering the steric hindrance and competitive adsorption of NP-15, i.e. adsorbed NP-15 on the interface will make the adsorption of TTAC difficult.

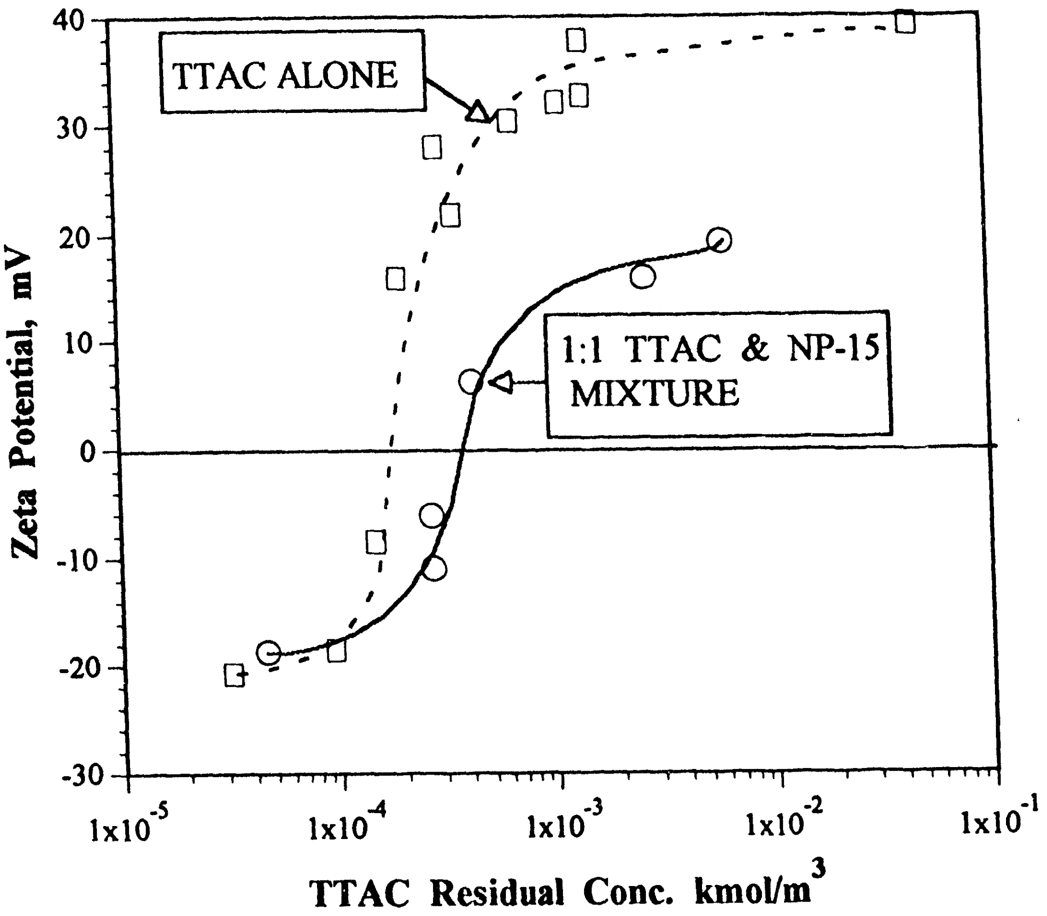


Figure 7. Zeta potential of alumina after adsorption of TTAC alone and after adsorption of 1:1 molar ratio surfactant mixture.

Figure 7 compares the zeta potential of alumina after adsorption from TTAC alone and from mixed surfactants. Since the maximum adsorption density of the cationic TTAC is lower in the mixed system, the plateau zeta potential at high concentration range is also lower. Interestingly, the isoelectric point (IEP) shifted to higher concentration (about 4×10^{-4} kmol/m^3) when adsorption was

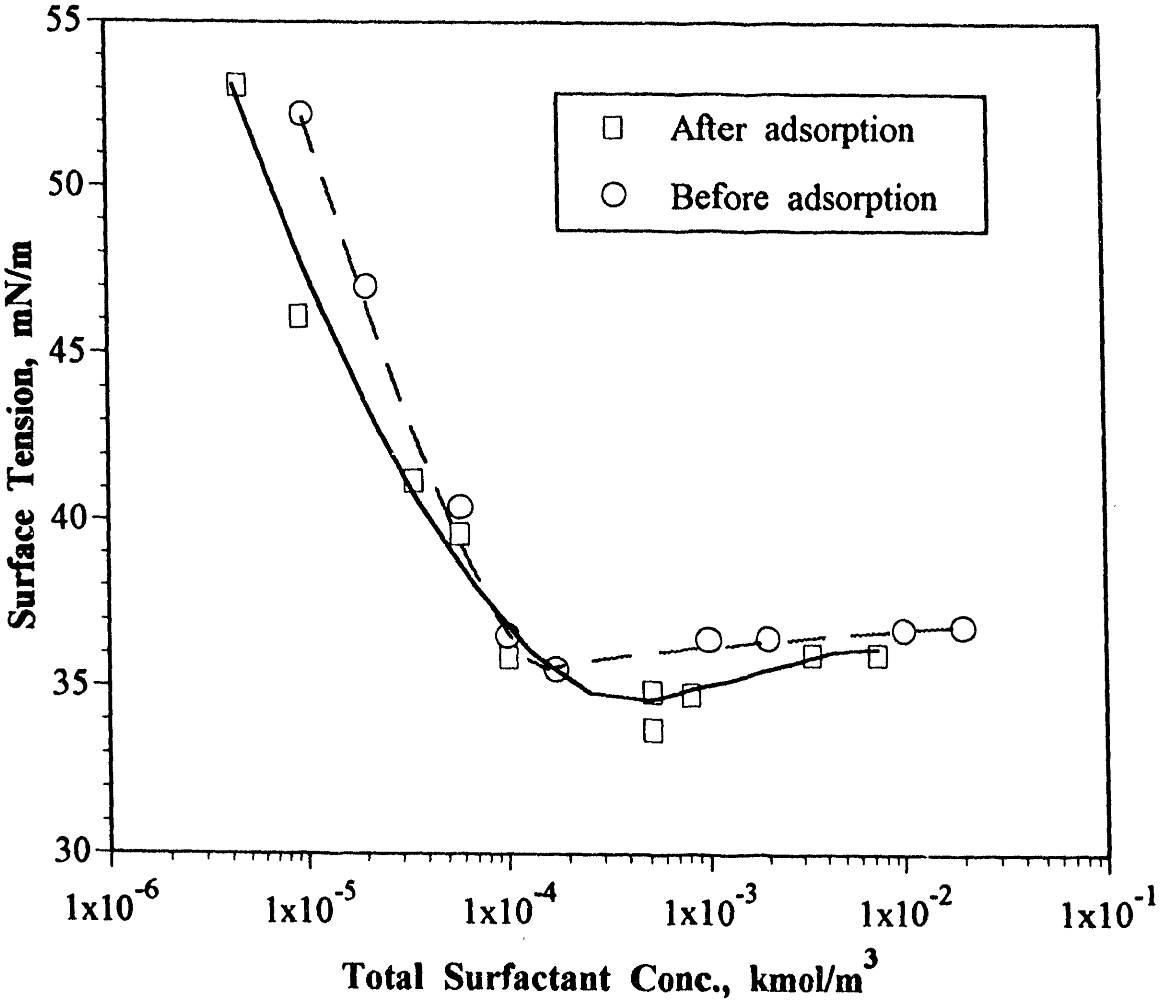


Figure 8. Surface Tension vs total surfactant concentration for 1:1 molar ratio mixture before and after contact with alumina

done from the mixed surfactant system. At this concentration the adsorption density of TTAC from the mixture is about $2x10^{-7}mol/m^2$, higher than the adsorption density from TTAC alone (about $1.5x10^{-8}mol/m^2$). The zeta potential of alumina after the adsorption of TTAC alone is higher than that after adsorption of 1:1 TTAC:NP-15 mixture. This indicates that the adsorption layer on alumina has a different structure and the positive charge of TTAC head is partially screened by the co-adsorbed NP-15.

The surface tension of the mixture was measured before and after adsorption and the results are shown in figure 8. The CMC of a 1:1 mixture of TTAC and NP-15 is about $1x10^{-4}kmol/m^3$ which is very similar to that of NP-15 alone($9.2x10^{-5}kmol/m^3$). After adsorption the CMC is shifted to a slightly higher concentration. There is a change in the surface tension isotherm, suggesting some preferential adsorption of one component over the other. Further investigation is needed for better understanding of the adsorption behavior of the mixed system.

Future work:

1. Adsorption/desorption of surfactant mixtures at alumina-water interface with different mixture ratio.
2. Calorimetric investigation of adsorption of mixed surfactants.
3. Effect of ethylene oxide chain length of C_nEO_n on SDS/C_nEO_n mixture adsorption.

Problem:

The study of thermodynamic parameters of surfactant adsorption and aggregation is behind schedule because of a problem with the microcalorimeter. Since the equipment is not manufactured in United States the spare parts had to be order from Sweden and has created a slight delay.

Reference:

1. Venable, R. L. and Nauman, R. V. , J. Phys. Chem. 68, 3498 (1964)

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